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GB 1271450   GB 0982872
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(54) **Synthetic zeolites**

(57) The invention concerns a preformed synthetic zeolite selected from the group consisting of Y, omega zeolite, offretite, erionite, L zeolite, ferrierite whose Si/Al atomic ratio r_f ranges from 1.5 to 100, the preformed synthetic zeolite being obtained from a preformed aluminosilicic material whose Si/Al atomic ratio r_i is lower than r_f and ranges from 0.5 to 90m by treating said material with a silica-containing product, in the presence of at least one organic or inorganic base.
The zeolite is particularly useful in sorption, in ionic mixing or in heterogeneous catalysis.
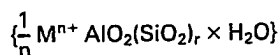
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SPECIFICATION

Synthetic zeolites

5 This invention relates to new synthetic zeolites.
   Zeolites are crystalline aluminosilicates generally complying with the general formula

$$\{\frac{1}{n} M^{n+} AlO_2(SiO_2)_r \times H_2O\}$$

10 wherein M is an alkali or alkaline-earth metal of valency n, and r is the atomic ratio of Si/Al. The structure
   comprises AlO_4 and SiO_4 tetrahedra interconnected through oxygen atoms. The structure defines a lattice of
   channels, cages and recesses. Cations M are at points in the structure where they can balance the negative
   charges carried by AlO_4 tetrahedra. Various arrangements of AlO_4 and SiO_4 tetrahedra are possible and
15 accordingly many different zeolite structures exist.
   This family of products has numerous industrial applications, particularly for adsorption and catalysis.
   In view of their high microporosity, zeolites may be used as adsorbents, e.g. for drying, separation of
   gaseous mixtures etc.
   The cations may be easily exchanged, thus making possible the preparation of acidic solids – usual form of
20 the zeolites for use as catalysts or catalyst components.
   Zeolites are generally obtained by admixing one or more silicon and aluminium sources with one or more
   inorganic or organic bases.
   They are mostly obtained as powders, the average particle size being generally smaller than 100 microns.
   For large scale use e.g. in adsorption or catalysis, shaped products are advantageous since fine powders
25 give rise to problems of pressure losses. Methods for zeolite powder agglomeration have been previously
   proposed, which generally require the addition of a binder used for shaping and giving a sufficient
   mechanical strength to the product. However, the purity of the product is decreased as a consequence of the
   addition of this binder which does not have the particular properties of the zeolite, so that the effectiveness
   of the shaped product is reduced.
30 The US Patent 3 119 660 discloses the preparation of zeolites from already shaped kaolin, in order to obtain
   preformed zeolites.
   We have now found it possible to prepare extrudates containing 100% zeolite and having improved
   mechanical strength. Conventional products, obtained by shaping zeolites with the addition of a binder,
   must contain the minimum binder amount in order to avoid a too substantial decrease of their activity, but
35 with the loss of mechanical strength. A compromise must be found between the degree of purity and
   mechanical strength. Mechanical strength is an essential parameter for an industrial product, used either for
   use as an adsorbent, or as a catalyst, either in the form of a fixed bed or a moving bed. Processes with
   moving catalyst beds occur more and more frequently in the refinery industry and require catalysts which
   are very resistant to attrition. Even in fixed bed processes, the mechanical strength must be sufficient to
40 avoid too high pressure drops in the unit. Moreover, catalyst regeneration is now more and more performed
   outside the unit, thus requiring repeated catalyst manipulation for which good mechanical properties are
   necessary.
   The invention provides a preformed synthetic zeolite selected from Y, omega, offretite, erionite, L and
   ferrierite zeolites, in which the Si/Al atomic ratio, r_f, is 1.5 to 100, and which has been obtained from at least
45 one preshaped aluminosilicic material selected from natural or synthetic zeolites, amorphous silica-
   aluminas and clays, said material having a Si/Al atomic ratio, r_i, lower than r_f and from 0.5 to 90, said
   preformed synthetic zeolite being produced by treating said material with a silica-containing product, in the
   presence of at least one organic or inorganic base selected from lithium oxide, sodium hydroxide, potassium
   hydroxide and tetraalkylammonium hydroxides, the OH^- anion concentration being 0.01 to 10 moles per
50 liter of solution, the molar ratio of tetraalkylammonium cations to $(OH)^-$ anions being 0. to 0.5, the amount of
   silica added to said material being 0.1 to 30 grams per gram of anhydrous aluminosilicic material, the liquid
   phase/anhydrous aluminosilicic material ratio, by weight, being 2 to 30, and said treatment being conducted
   at a temperature of from 50 to 200°C, for a period of from 2 hours to about 200 days.
   The zeolites of the present invention contain no binder and have excellent mechanical properties, as
55 shown particularly by the measured values of the crushing strength and of the attrition (by a method
   hereinafter defined), values which could difficultly be obtained by conventional shaping methods.
   The invention allows the production of zeolites of small crystallites size. It may be advantageous e.g. for a
   catalytic application to use a zeolite consisting of very fine particles, for example of average size of from 0.1
   to 0.3 microns. Such a product would generally not raise serious crystallization problems, but the separation
60 of crystals from synthesis mother liquors would be extremely difficult, and the time-consuming filtration or
   centrifugation would be an obstacle to the industrial production of this type of product.
   The method of the present invention is free of these problems and directly provides zeolites of very small
   crystalline size incompatible with a synthesis in powder form.
   The invention thus provides simultaneously for shaped zeolites of high mechanical strength, consisting of
65 100% pure zeolite, and zeolite whose crystalline size are generally smaller than are micro.

Zeolites may be identified by different characterizing methods, e.g. chemical analysis, X-ray diffraction, adsorption of various molecules such as n-hexane and cyclohexane; moreover, the crystaline size may be estimated by scanning electron microscopy and the mechanical strength by measurement of attrition and crushing.

5   The silica and alumina contents, as well as the cation rates may be determined by chemical analysis.   5

X-Ray diffraction determines distances "d" between lattice planes of the crystals, as well as the relative intensities corresponding to each distance, said relative intensities being expressed with respect to the most intense line of the pattern. Distance-intensity pairs are characteristic of each zeolite, although slight modifications may occur, depending on the cations present in the structure.

10   Adsorption capacities may be determined in a conventional apparatus of the MacBain type. Zeolites are   10
activated under a pressure of 5 torrs, at about 400°C. Then, the sample is contacted, at the desired
temperature, often 20°C, with the product to adsorb at a known partial pressure.

The crystalline size may be estimated by scanning electron microscopy according to the following procedure. After crushing of the grain, the powder is deposited on a sample carrier, then metal-plated with

15   gold and introduced in a microscope of the Camebax type, of CAMECA company.   15

Conveniently, two tests of mechanical strength may be performed: one consists of measuring the crushing grain by grain and the other of measuring the attrition.

Crushing strength is determined by applying a progressively increasing charge to the grain. The apparatus used may be atomic press with a movable piston known by the ERWEKA trade mark. The measurement is

20   effected on 30 grains and the arithmetic means value is calculated. For extrudates, the value is the ratio of the   20
crushing strength required for breaking, expressed in kilograms (or in Newtons), to the length of the extrudate, expressed in millimeters.

A second test for estimating the mechanical properties of the product consists of measuring the attrition of a bed of grains in reaction with the pressure applied to said bed. The operating mode is as follows : 20 cc of

25   grains are formed into a cylinder of 50 mm height and 27.6 mm internal diameter. The grains are covered   25
with 5 cc of steel balls of 4.5 mm thickness. The pressure applied to these balls, by means of a piston, increases by steps. The fines obtained at different pressures are separated by screening and weighed. Fines are considered to be the particles passing through sieve meshes whose opening is equal to 2/3 of the minor characteristic size of the initial grain. The resistance to crushing corresponds to the value of the pressure,

30   expressed in Megapascals, at which 0.5 % of fines are obtained, said value being determined by   30
interpolation on a diagram giving the proportion of fines obtained at various pressures.

The present invention concerns synthetic performed zeolites selected from the group consisting of Y zeolite, omega zeolite, offretite, erionite, L zeolite, ferrierite, these zeolites being prepared from a starting raw material based on at least one product containing at least aluminium or silicon. This starting product may be

35   crystalline or amorphous. It may consist of a crystallized zeolite or a zeolite made amorphous by a previous   35
treatment, said zeolite being either natural or synthetic and of any crystallite size.

Examples of natural zeolites are analcite, chabazite, clinoptilolite, erionite, faujasite, ferrierite and mordenite; these zeolites are rarely of high purity and are generally found as mixtures and associated with amorphous products. It may be of interest to directly use them as crushed particles obtained by ore crushing.

40   Examples of synthetic zeolites are A zeolite, X and Y zeolites, mordenite.   40

Optionally, other zeolites may be used, provided that their Si/Al atomic ratio is lower than that of the product to be obtained. X-Ray diffraction spectra of X and Y faujasites are respectively given in French Patents 1 117 756 and 1 231 239.

The mordenite diffraction spectrum is given in the paper of SAND and coll : Adv. Chem. Ser. ACS.

45   WASHINGTON DC (1971), 101 page 12. The diffraction spectrum of A zeolite is given in US Patent 2 882 243.   45

All these zeolites may be exchanged at least partially with other cations than their original cations, such as K^+, Li^+ NH_4^+, H^+, the exchange rates being variable from 0 to 100%.

These zeolites may also be modified by a treatment for aluminum removal, according to conventional methods of the prior art.

50   It is also possible to use, as starting raw material, extrudates or pellets or balls or other forms of   50
amorphous synthetic silica-alumina ; these products may be synthesized for this purpose and are commercially available.

A clay, of the kaolin or metakaolin type may also be used.

It is also possible to use a mixture of the above-mentioned products. In particular, zeolites are easily

55   shaped by means of a binder which may consist, for example, of an alumina or a clay.   55

According to the invention, and in order to obtain a preformed synthetic zeolite, the preformed product is contacted with at least one organic or inorganic liquid base selected from lithium oxide, potassium hydroxide, sodium hydroxide, ammonia and tetraalkyl-ammonium hydroxides, for example tetramethyl or ethyl or propyl or butyl ammonium hydroxides.

60   To this reaction medium, comprising the preformed material, whose Si/Al atomic ratio is equal to r_i, and at 60
least one liquid base, is added at least one silica-containing product, which may for example comprise an amorphous silica or a colloidal silica, in order to obtain a preformed zeolite having a Si/Al ratio r_f, greater than r_i. The so-obtained preformed zeolite has an excellent mechanical strength.

The conditions used for synthesis of these preformed zeolites are conveniently as follows: the Si/Al atomic ratio r_i of the starting preformed material should range from 0.5 to 90 ; the concentration of $(OH)^-$ anions of the base should range from 0.01 to 10 moles per liter of the solution ; the molar ratio of tetraalkylammonium cations to $(OH)^-$ anions ranges from 0 to 0.5. The silica amount used should be from 0.1 to 30 grams per
5 gram of anhydrous aluminosilicic material used. The ratio by weight of the liquid phase to the starting preformed aluminosilicate should be from 2 to 30 ; the treatment temperature ranges from 50 to 200°C; the treatment time should be 2 hours to about 200 days.

The Si/Al atomic ratio r_f of the obtained zeolite should generally be higher than the ratio r_i, in the range of 1.5 to 100. Among the products which can be obtained according to the invention, particular examples are Y
10 and omega zeolites, offretite erionite, L zeolite and ferrierite.

Y zeolite is characterized by a lattice of 3-dimensional channels whose opening is about 8 Å $(8.10^{-10}m)$. It is generally obtained in sodium form with a Si/Al atomic ratio from 1.5 to 3 and preferably from 2.0 to 2.7. Its X-ray diffraction diagram is given in Table 1 (extract from USP 3 130 007); d is the distance between two lattice planes, expressed in meters, and I/I_o (or I/I_{max}) the ratio, expressed in percent, of the intensity of any
15 given line I to the intensity of the most intense line I_o or I_{max}. The only lines considered are those corresponding to ratios I/I_{max} or I/I_o higher than 10. Of course, distances d, as well as ratios I/I_o may be subject to small variations according to the product considered. Modifications do not indicate a change of structure but are due to the replacement of certain cations with others or to a deviation of the Si/Al ratio.

TABLE 1

d (meters)	I/I_o
14.29×10^{-10}	100
7.46×10^{-10}	24
5.68×10^{-10}	44
4.76×10^{-10}	23
4.38×10^{-10}	35
3.91×10^{-10}	12
3.77×10^{-10}	47
3.31×10^{-10}	37
3.02×10^{-10}	16
2.92×10^{-10}	21
2.86×10^{-10}	48
2.77×10^{-10}	20
2.64×10^{-10}	19
2.59×10^{-10}	11

40   Omega zeolite has a lattice of monodimensional channels with an opening of about 8 Å ; it generally contains less Na^+ ions and has a Si/Al atomic ratio generally from 2 to 6.

Its diffraction diagram, giving the distances corresponding to the most intense lines is given in Table 2 (extract from USP 3 578 723).

TABLE 2

d (meters)	I/I_o (%)
16.0×10^{10}	20
9.18×10^{-10}	100
7.96×10^{-10}	20
6.94×10^{-10}	30
6.01×10^{-10}	33
4.73×10^{-10}	31
3.97×10^{-10}	11
3.82×10^{-10}	69
3.74×10^{-10}	28
3.64×10^{-10}	26
3.54×10^{-10}	54
3.46×10^{-10}	14
3.17×10^{-10}	48
3.10×10^{-10}	23
3.05×10^{-10}	21
2.99×10^{-10}	13
2.93×10^{-10}	28

Offretite zeolite has a lattice of monodimensional channels having an opening of about 6.5 Å, as well as a narrower lattice perpendicular to the first one. It is generally synthetized with at least potassium cations and a Si/Al atomic ratio from 2 to 8 for the present invention. Its diffraction diagram, showing the distances corresponding to the most intense lines, is given in Table 3.

TABLE 3

d (meters)	I/I_o (%)
11.45×10^{-10}	100
7.54×10^{-10}	17
6.63×10^{-10}	55
6.30×10^{-10}	10
5.74×10^{-10}	15
4.57×10^{-10}	27
4.34×10^{-10}	43
3.76×10^{-10}	89
3.59×10^{-10}	43
3.31×10^{-10}	19
3.15×10^{-10}	17
2.93×10^{-10}	10
2.85×10^{-10}	80
2.68×10^{-10}	19
2.51×10^{-10}	14

Erionite is a structure related to offretite, but with different plane stacking arrangements. The stacking sequences are regular for pure erionite ; irregular stacking sequences related to defects in a structure containing offretite, correspond to T erionite. It has a pore lattice with an opening from 4 to 5 A; the Si/A1 atomic ratio may vary from 2 to 6 for the present invention. Its X-ray diffraction diagram (most intense lines) is given in Table 4 (extract from USP 2 950 952).

TABLE 4

d (meters)	I/I_o (%)
11.45×10^{-10}	100
7.54×10^{-10}	13
6.63×10^{-10}	54
4.34×10^{-10}	45
3.82×10^{-10}	16
3.76×10^{-10}	56
3.59×10^{-10}	30
3.31×10^{-10}	16
3.18×10^{-10}	12
3.15×10^{-10}	18
2.93×10^{-10}	11
2.87×10^{-10}	38
2.85×10^{-10}	45

L-zeolite is a zeolite having a pore opening of about 6.5–7 Å and a Si/Al atomic ratio generally from 2 to 4. Its X-ray diffraction spectrum (most intense lines) is given in Table 5 (extract from USP 3 216 789).

TABLE 5

d (meters)	I/I_o (%)
5.59×10^{-10}	100
11.20×10^{-10}	14
11.81×10^{-10}	15
14.80×10^{-10}	25
15.40×10^{-10}	11
19.41×10^{-10}	32
20.21×10^{-10}	13
20.49×10^{-10}	13
22.72×10^{-10}	30
23.52×10^{-10}	13
24.30×10^{-10}	19
25.58×10^{-10}	23
27.33×10^{-10}	14
28.13×10^{-10}	34
29.06×10^{-10}	22
29.55×10^{-10}	15
30.70×10^{-10}	23
33.80×10^{-10}	19

25   Ferrierite is a zeolite of pore opening from about 5 to 5.5 Å and of Si/Al ratio generally from 3 to 100 for the present invention (atomic ratio). Its X-ray diffraction spectrum (most intense lines) is given in Table 6 (extract USP 4 017 590).

TABLE 6

d (meters)	I/I_o (%)
9.55×10^{-10}	75
7.13×10^{-10}	52
6.65×10^{-10}	25
5.75×10^{-10}	20
5.69×10^{-10}	23
3.99×10^{-10}	43
3.93×10^{-10}	30
3.78×10^{-10}	54
3.65×10^{-10}	33
3.55×10^{-10}	100
3.48×10^{-10}	92
3.32×10^{-10}	21
3.13×10^{-10}	42
3.03×10^{-10}	32
2.48×10^{-10}	10

50   Tables 8 to 13 give the operating characteristics required for preparing preformed synthetic zeolites according to the invention and the main characteristics of these synthetic zeolites (wide and preferred ranges). Table 8 concerns the production of Y faujasite, Table 9 the production of omega zeolite, Table 10 the production of offretite, Table 11 the production of erionite, Table 12 the production of L zeolite and Table 13 the production of ferrierite.

TABLE 7

SYNTHESIS PARAMETERS

r_i Si/Al atomic ratio of starting preformed aluminosilicate.

B Selected base

S_1 Ratio by weight liquid phase/starting preformed alumino-silicate

S_2 $(OH)^-$ ions concentration (mole/liter).

S_3 Molar ratio tetraalkylammonium cations/OH^- anions.

Q Silica amount involved, in grams, of dry silica per gram of starting preformed dry aluminosilicate.

T Temperature (°C).

t Time of treatment of the aluminosilicate preformed by the basic solution and the silica (in days).

d Size of the obtained zeolite elementary crystals, in microns.

r_f Si/Al atomic ratio of the obtained zeolite.

TABLE 8

Characteristic features in the production of Y faujasite

Initial preformed alumino-silicate	r_i		S_1		S_2		S_3		Q	
	wide range	pre-fer-red	wide range	pre-fer-red	wide ran-	pre-fer-red	wide range	pre-fer-red	wide range	pre-fer-red
A	0.8 to 1.4	0.9 to 1.2	2 to 30	2 to 25	0.2 to 10	1 to 8	0 to 0.1	0 to 0.05	0.1 to 30	0.5 to 20
X	0.9 to 1.6	1 to 1.5	"	"	"	"	"	"	"	"
Amorphous silica alumina	0.5 to 2.7	0.8 to 2.5	"	"	"	"	"	"	"	"
Kaolin	0.9 to 1.1	0.9 to 1.1	"	"	"	"	"	"	"	"

T		t		d		r_f		B
wide range	pre-fer-red	wide range	pre-fer-red	wide range	pre-fer-red	wide range	pre-fer-red	
60 to 120	80 to 100	1 to 20	3 to 10	0.02 to 50	0.1 to 10	1.5 to 3	2 to 2.7	.NaOH
"	"	"	"	"	"	"	"	.NaOH+LiOH
20 to 140	40 to 110	0.1 to 200	0.2 to 40	"	"	"	"	Tetra-alkyl-ammonium hydroxides
"	"	"	"	"	"	"	"	

TABLE 9

Characteristic features in the production of omega zeolite

Initial preformed alumino-silicate	r_i wide range	r_i preferred	S_1 wide range	S_1 preferred	S_2 wide range	S_2 preferred	S_3 wide range	S_3 preferred	Q wide range	Q preferred
A	0.8 to 1.4	0.9 to 1.2	2 to 30	3 to 25	0.1 to 10	0.2 to 8	0.01 to 0.3	0.01 to 0.2	0.1 to 30	0.5 to 20
X	0.9 to 1.6	1 to 1.5	"	"	"	"	"	"	"	"
Y	1.6 to 3.2	1.7 to 3	"	"	"	"	"	"	"	"
Amorphous silica alumina	0.5 to 5	0.8 to 4	"	"	"	"	"	"	"	"
Kaolin	0.9 to 1.1	0.9 to 1.1	"	"	"	"	"	"	"	"

T wide range	T preferred	t wide range	t preferred	d wide range	d preferred	r_f wide range	r_f preferred	B
100 to 200	140 to 180	0.5 to 10	0.8 to 5	0.02 to 50	0.05 to 10	2 to 6	3 to 5	.NaOH
"	"	"	"	"	"	"	"	.NaOH+KOH
"	"	"	"	"	"	"	"	.NaOH+LiOH
"	"	"	"	"	"	"	"	.NaOH+KOH+LiOH
20 to 200	40 to 180	0.1 to 200	0.2 to 40	"	"	"	"	Tetra-alkyl-ammonium hydroxides
"	"	"	"	"	"	"	"	

TABLE 10

Characteristic features in the production of offretite zeolite

Initial preformed alumino-silicate	r_i wide range	r_i preferred	S_1 wide range	S_1 preferred	S_2 wide range	S_2 preferred	S_3 wide range	S_3 preferred	Q wide range	Q preferred
A	0.8 to 1.4	0.9 to 1.2	2 to 30	3 to 25	0.1 to 10	0.2 to 8	0.01 to 0.5	0.01 to 0.3	0.1 to 30	0.5 to 20
X	9.0 to 1.6	1 to 1.5	"	"	"	"	"	"	"	"
Y	1.6 to 3.2	1.7 to 3	"	"	"	"	"	"	"	"
Amorphous silica alumina	0.5 to 5	0.8 to 4	"	"	"	"	"	"	"	"
Kaolin	0.9 to 1.1	0.9 to 1.1	"	"	"	"	"	"	"	"

T wide range	T preferred	t wide range	t preferred	d wide range	d preferred	r_f wide range	r_f preferred	B
100 to 200	140 to 180	0.5 to 10	0.8 to 8	0.02 to 50	0.1 to 10	2 to 8	3 to 7	.KOH
"	"	"	"	"	"	"	"	.KOH+ NaOH
"	"	"	"	"	"	"	"	.KOH+ LiOH
20 to 200	40 to 180	0.1 to 200	0.2 to 40	"	"	"	"	.KOH+ NaOH+ LiOH Tetra-alkyl-ammonium
"	"	"	"	"	"	"	"	hydroxides

TABLE 11

Characteristic features in the production of erionite zeolite

Initial preformed aluminosilicate	r_I wide range	r_I preferred	S_1 wide range	S_1 preferred	S_2 wide range	S_2 preferred	S_3 wide range	S_3 preferred	Q wide range	Q preferred
A	0.8 to 1.4	0.9 to 1.2	2 to 30	3 to 25	0.1 to 10	0.2 to 8	0 to 0.01	0 to 0.008	0.1 to 30	0.5 to 20
X	0.9 to 1.6	1 to 1.5	"	"	"	"	"	"	"	"
Y	1.6 to 3.2	1.7 to 3	"	"	"	"	"	"	"	"
Amorphous silica alumina	0.5 to 5	0.8 to 4	"	"	"	"	"	"	"	"
Kaolin	0.9 to 1.1	0.9 to 1.1	"	"	"	"	"	"	"	"

T wide range	T preferred	t wide range	t preferred	d wide range	d preferred	r_f wide range	r_f preferred	B
100 to 200	140 to 180	0.5 to 8	0.8 to 5	0.02 to 50	0.1 to 10	2 to 6	3 to 5	.KOH .KOH+ NaOH
"	"	"	"	"	"	"	"	.KOH+ LiOH
								.KOH+ NaOH+ LiOH
"	"	"	"	"	"	"	"	.Tetra- alkyl- ammonium hydroxides
20 to 200	40 to 180	0.1 to 200	0.2 to 40	"	"	"	"	
"	"	"	"	"	"	"	"	

TABLE 12

Characteristic features in the production of L zeolite

Initial preformed alumino-silicate	r_i wide range	r_i preferred	S_1 wide range	S_1 preferred	S_2 wide range	S_2 preferred	S_3 wide range	S_3 preferred	Q wide range	Q preferred
A	0.8 to 1.4	0.9 to 1.2	2 to 30	3 to 25	0.1 to 10	0.2 to 8	0 to 0.5	0 to 0.01	0.1 to 30	0.5 to 20
X	0.9 to 1.6	1 to 1.5	"	"	"	"	"	"	"	"
Y	1.6 to 3.2	1.7 to 3	"	"	"	"	"	"	"	"
Amorphous silica alumina	0.5 to 3.5	0.8 to 3	"	"	"	"	"	"	"	"
Kaolin	0.9 to 1.1	0.9 to 1.1	"	"	"	"	"	"	"	"

T wide range	T preferred	t wide range	t preferred	d wide range	d preferred	r_f wide range	r_f preferred	B
50 to 200	70 to 180	0.5 to 10	0.8 to 8	0.01 to 10	0.05 to 5	2 to 4	2.5 to 3.5	.KOH
"	"	"	"	"	"	"	"	.KOH+ NaOH
"	"	"	"	"	"	"	"	.KOH+ LiOH
"	"	"	"	"	"	"	"	.KOH+ NaOH+ LiCH
"	"	"	"	"	"	"	"	Tetra-alkyl-ammonium hydroxides

TABLE 13

Characteristic features in the production of ferrierite zeolite

Initial preformed aluminosilicate	r_i		S_1		S_2		S_3		Q	
	wide range	preferred	wide range	preferred	wide range	preferred	wide range	preferred	wide range	preferred
A	0.8 to 1.4	0.9 to 1.2	2 to 30	3 to 25	0.01 to 5	0.1 to 4	0.01 to 0.4	0.01 to 0.3	0.1 to 30	0.5 to 20
X	0.9 to 1.6	1 to 1.5	"	"	"	"	"	"	"	"
Y	1.6 to 3.2	1.7 to 3	"	"	"	"	"	"	"	"
Mordenite	4 to 6.5	4.5 to 6	"	"	"	"	"	"	"	"
Amorphous silica alumina	0.5 to 90	0.8 to 35	"	"	"	"	"	"	0.1 to 50	0.2 to 30
Kaolin	0.9 to 1.1	0.9 to 1.1	"	"	"	"	"	"	0.1 to 30	0.5 to 20

T		t		d		r_f		B
wide range	preferred	wide range	preferred	wide range	preferred	wide range	preferred	
180 to 350	200 to 350	0.1 to 5	0.2 to 2	0.01 to 50	0.05 to 10	3 to 100	4 to 40	.NaOH
"	"	"	"	"	"	"	"	.NaOH+ LiCH
"	"	"	"	"	"	"	"	Tetra-alkyl-ammonium hydroxides
"	"	"	"	"	"	"	"	
"	"	"	"	"	"	"	"	
"	"	"	"	"	"	"	"	

The so-obtained synthetic zeolites may be used in applications concerning for example adsorption, heterogenous catalysis and cationic exchange.

They may be used as such, but generally they are subjected to certain modifications required for the expected use, for example to at least one pretreatment. Examples of pretreatments to which it may be
5 necessary to subject these preformed synthetic zeolites are : cationic exchanges, thermal treatments with,   5
for example, different roasting atmospheres. The zeolite obtained after synthesis and washing may be roasted, particularly for removing organic cations optionally used for synthesis and still present in the structure, for example of the tetrapropylammonium or tetrabutylammonium type. For applications in sorption, catalysis or cationic exchange, these preformed synthetic zeolites may be exchanged with any
10 other possible cation. Particularly for catalytic uses, and mainly in acid catalysis, it may be advantageous to   10
remove the alkali cations present in the structure and to replace them with protons, this being commonly performed by one or more cationic exchanges with ionizable ammonium salts such as nitrate, sulfate, chloride, acetate or equivalents; the ammonia will then be removed by roasting with or without steam, with or without gas scavenging, in a temperature range from 300 to 900°C. The treatments may lead to zeolites
15 modifications known in the prior art and called stabilization and ultra-stabilization treatments. It is also   15
possible to obtain zeolites in protonic form, to proceed to treatments with organic or inorganic acids which, in addition, may partially or completely remove aluminum from the crystal lattice. Aluminum removal may also be achieved with chelating agents or by treatment in vapor phase with silicium tetrachloride, hydrochloric acid or other equivalent compounds.
20 It may be also of interest to introduce other cations, particularly alkaline-earth cations, rare-earth cations or   20
cations from metals of VIB, VIIB, IB, IIB, IIIA, IVA, VA, VIA groups.

For catalytic uses requiring bifunctional catalysts, i.e. associating an acid function with a metal function (so-called active phase), one or more metal or metalloid compound(s) can be introduced by methods known in the prior art, which may consist of cationic exchange, dry impregnation, steam deposition etc... The metal
25 or metalloid precursor compound may optionally be introduced during the synthesis of the preformed   25
zeolite.

This type of shaped zeolites have many applications in sorption, ionic exchange and catalysis.

In particular, the zeolites according to the invention are well adapted to catalytic uses : thus, in order to improve the behaviour at cold of a gas-oil cut, it may be advantageous to subject this cut to a treatment
30 under hydrogen pressure over a catalyst as prepared according to the invention. This catalysts may contain   30
at least one noble or non noble metal from group VIII and/or one metal from other group(s) of the periodic classification of elements, the catalyst carrier comprising for example offretite, ferrierite or erionite, the preferred zeolites being offretite and ferrierite. As a general rule, these types of catalysts are convenient in catalytic cracking reactions, in the presence or absence of a matrix or of another solid compound.
35 Another application concerns the improvement of the gasolines octane number by cracking the normal   35
paraffins contained in the mixture. The quality of a reformate may be improved by catalytic treatment with the zeolites prepared according to the invention. The catalyst will consist of offretite, ferrierite or erionite, the preferred zeolites being ferrierite and erionite, containing optionally small amounts of at least one noble or non noble metal from group VIII.
40 The reactions of aromatics conversion are also advantageously performed by using zeolites prepared   40
according to the invention; examples of such reactions are : toluene dismutation xylenes isomerization, toluene-methanol alkylation, benzene-ethylene alkylation.

The hydrocracking of middle of heavy cuts may be advantageously performed in the presence of zeolites prepared according to the invention. The catalyst must contain a metal from group VIII, optionally associated
45 with a metal from group VIB. The process is performed under a hydrogen pressure from 20 to 200 bars and at   45
a temperature from 220 to 450°C.

Methanol conversion is also possible with the use of a catalyst whose carrier contains at least one of the zeolites prepared according to the invention. This reaction is performed under a pressure of 10 bars and at a temperature from 300 to 550°C, to produce methanol condensation compounds. The process may be
50 optimized for synthesizing either light olefins comprising essentially 2 to 4 carbon atoms per molecule, or a   50
mixture useful as motor fuel.

Dehydrocyclization of paraffins is also an application of the invention. It may be advantageously performed on a L zeolite synthesized according to the invention and containing potassium ions in majority. It is desirable to introduce at least one metal from group VIII, preferably platinum, optionally associated with
55 another metal, for example from group VIIB. The catalyst is used in conditions close to those of catalytic   55
reforming and with a charge containing a high proportion of paraffins, so as to obtain effluents of high aromatics content.

EXAMPLES
The following non-limiting examples illustrate the present invention.

Example 1 : Preparation of Y zeolite (Y faujasite)
5 *Method 1*
    230 g of colloidal silica of 40 % by weight silica content and 670 ml of sodium hydroxide at a 2.1 M
concentration are added to 40 g of A zeolite extrudates (r_i = 0.95). The synthesis parameters (see tables 7 and
8) are as follows : S_1 = 21.35 ; S_2 = 1.65 mole/liter ; S_3 = 0 ; Q = 0.95). The synthesis parameters (see tables 7
and 8) are as follows : S_1 = 21.35 ; S_2 = 1.65 mole/liter ; S_3 = 0 ; Q = 2.3. After 7 days of heating at 100°C, the
10 extrudates are filtered, washed and dried. As shown by X-ray diffraction, they consist of Y faujasite having a   10
Si/Al atomic ratio, r_f, of 2.65. The crushing strength grain by grain is 18.3 Newton/mm and the crushing
strength in bed 1.3 MPa, as compared respectively to 3.3 N/mm and 0.9 MPa for zeolite. The benzene
adsorption capacity of 30°C and with a partial pressure of 35 torrs, of the sample desorbed under vacuum at
300°C is 20.4 % by weight. The BET specific surface is 880 m^2/g. The crystallites size, as determined by
15 microscopy, is about 0.3 micron.   15

Method 2
    819 g of water, 75 g of pelletized sodium hydroxide and 227 g of colloidal silica of 40 % by weight silica
content are added to 63 g of amorphous extrudates containing 70 % of silica and 30% of alumina (r_i 1.98). The
20 synthesis parameters are as follows (see table 7 and 8) : S_1 = 15.16 ; S_2 = 1.96 ; S_3 = 0 and Q = 1.44. After 5   20
days of maturation at 40°C, the mixture is brought to 100°C for 24 hours. The extrudates are then filtered,
washed and dried. The diffraction spectrum corresponds to that of Y faujasite (r_f = 2.30).

Method 3
25   50 g of kaolinite extrudates (r_i = 1) are admixed with 280 g of colloidal silica of 40 % by weight silica   25
content, 70 g of sodium hydroxide and 840 ml of water. The synthesis parameters are as follows (see tables 7
and 8) : S_1 = 20.16; S_2 = 1.74 ; S_3 = 0 and Q = 2.24. After one day of maturation at 40°C and 5 days of heating
at 100°C, the product is filtered, washed and dried. The diffraction spectrum corresponds to that of Y zeolite
(r_f = 1.245).
30   30

Example 2 : Preparation of omega zeolite
Method 1
    5 g of 4 A zeolite extrudates (r_i = 1) are added to 105 ml of a solution containing, by weight, respectively,
6.1%, 1.68%, 31.8% of sodium hydroxide, tetramethylammonium hydroxide and silica. The synthesis
35 parameters, in accordance with table 9 are as follows : S_1 = 21.0 ; S_2 = 2.38 moles/liter ; S_3 = 0.106 ; Q = 9.32   35
g/g.
    After 24 hours of heating at 170°C, the extrudates are filtered, washed, dried and roasted at 600°C. Thus, 9.4
g of omega zeolite extrudates having a Si/Al atomic ratio (r_f) of 3.54 are obtained. X-ray diffraction shows
their high purity.
40   The grain by grain crushing strength is 21.2 Newton/mm and the crushing strength in bed of 1.4 MPa, as   40
compared with respectively 8.3 Newton/mm and 0.9 MPa, for 4 A zeolite.
    The size of the zeolite elementary crystals, as determined by scanning electron microscopy, is from 0.08 to
0.8 micron.

45 *Method 2*   45
    3.76 of amorphous silica, 1.76 g of pelletized sodium hydroxide and 32 ml of a 0.13 M tetramethylammo-
nium hydroxide solution are added to 2.5 g of Na Y zeolite extrudates whose r_i ratio is equal to 2.6. The
synthesis parameters are as follows : S_1 = 12.8 ; S_2 = 1.51 mole/liter ; S_3 = 0.086 ; Q = 1.50 g/g.
    The so-prepared mixture is heated at 170°C for 36 hours in autoclave. 3.7 g of omega zeolite (r_f = 3.7) are
50 obtained after filtration, washing and drying.   50

Method 3
    5 g of kaolinite extrudates (r_i = 1) are added to 95 ml of a solution containing respectively 6 %, 1.5%, 30% of
sodium hydroxide, tetramethylammonium hydroxide and silica. The synthesis parameters are as follows :
55 S_1 = 19.0 ; S_2 = 1.67 ; S_3 = 0.099 ; Q = 7.83. After 24 hours of heating at 170°C, the extrudates are filtered,   55
washed, dried and roasted at 600°C. The crushing strength grain by grain is 21.9 N/m and the crushing
strength in bed 1.4 MPa, as compared respectively with 9.9 N/mm and 0.9 MPa for the starting kaolinite (r_f =
3.8).

Example 3 : Preparation of offretite
Method 1

50 g of Na Y zeolite extrudates having a Si/Al atomic ratio of 2.5 are suspended into 200 ml of ammonium nitrate molar solution, at 80°C, for 14 hours. After filtration and washing, this operation is repeated twice. The
5 solid phase is then separated from the solution, washed with water and dried at 100°C for 4 hours. After 3   5
hours of roasting at 550°C, 41 g of HY zeolite extrudates are obtained.

25 g of a 2 M potassium hydroxide solution, 5 ml of a 20 % by weight tetramethylammonium hydroxide solution and 7.5 g of colloidal silica containing 40 % by weight of silica are added to 2.5 g of HY zeolite.

The synthesis parameters, in conformity with table 10, are as follows : S_1 = 14.4; S_2 = 1.69 mole/liter ; S_3 =
10 0.179 ; Q = 1.2 g/g.   10

The whole mixture is heated at 170°C for 24 hours in autoclave. After cooling, the extrudates are filtered, washed with water, dried at 100°C for 3 hours, and finally roasted for 3 hours at 550°C. The so-prepared extrudates have a diffraction diagram similar to that of offretite and a Si/Al atomic ratio (r_f) of 4.5. The average value of the grain by grain crushing strength is 10.6 Newton/mm ; it was 5.3 for the starting NaY
15 zeolite. The crushing strength in bed is 1.58 MPa as compared with 1.05 for the starting product. The   15
cyclohexane adsorption capacity is 6.5% by weight at 20°C under a pressure of 65 torrs. After 4 successive cationic exchanges in ammonium nitrate solutions, followed with a roasting at 500°C, the adsorption capacity is 8.9 % by weight, thus attesting the high purity of the product. The potassium content is then 2.1 %.
20   Scanning electron microscopy shows that the average size of zeolite elementary crystals is about 0.3   20
micron.

Method 2

100 g of 4 A zeolite extrudates of Si/Al atomic ratio (r_i) equal to 1, are exchanged three times with 500 ml of
25 a molar ammonium acetate solution at 60°C for 24 hours. After washing with water and drying for 3 hours at   25
100°C, the extrudates are roasted for 4 hours at 500°C. Thus, 87 g of extrudates are obtained. The synthesis parameters are as follows : S_1 = 21.5 ; S_2 = 3.02 ; S_3 = 0.19 ; Q = 9.75.

40 g of these extrudates are added to 860 ml of a solution containing 9.1 %, 3.46 %, 31.5%, respectively of potassium hydroxide, tetramethylammonium hydroxide and silica. After 24 hours of heating at 170°C in
30 autoclave, the extrudates are filtered, washed dried and roasted at 550°C for 4 hours. Thus, 84 g of offretite   30
are obtained which adsorb 6.8 % by weight of cyclohexane at 20°C under 65 mm of mercury.

The average value of the grain by grain crushing strength is 29 Newton/mm, as compared with 8.3 Newton/mm for 4 A zeolite. The resistance to crushing in bed is 1.6 MPa, as compared to 0.9 MPa for 4 A zeolite (r_f = 3.85).
35   35
Method 3

24 g of potassium hydroxide, 1.95 g of tetramethylammonium chloride, 29 g of amorphous silica and 40 ml of water are added to 5 g of kaolin (r_i = 1) (synthesis parameters : S_1 = 8; S_2 = 4.89 ; S_3 = 0.091 ; Q = 5.8). The mixture is brought to 170°C for 24 hours and the obtained extrudates are filtered, washed and dried. 9.1
40 g of offretite adsorbing 8.2 % of n-hexane at 20°C under 95 mm of mercury (r_f = 3.8) are thus obtained. The   40
grain crushing strength is 23 N/mm, and the crushing in bed of 1.4 MPa, as compared respectively with 9.9 N/mm and 0.9 MPa for the starting kaolin.

Method 4
45   44g of water, 6.21 g of amorphous silica, 5.23 g of potassium hydroxide, 1.6 g of tetramethylammonium   45
chloride are added to 2.5 g of NaX zeolite extrudates having a Si/Al ratio, r_i, equal to 1.1 and the mixture is then heated at 170°C for 24 hours. After filtration, washing and drying, offretite extrudates are obtained with a Si/Al ratio (r_f) equal to 3.9. The synthesis parameters were as follows : S_1 = 17.6 ; S_2 = 2.45 ; S_3 = 0.135 ; Q = 2.48.
50   50
Method 5

3.7 g of sodium hydroxide, 2.15 g of potassium hydroxide, 6 ml of a 10% by weight tetramethylammonium hydroxide solution and 16.4 g of colloidal silica of 40 % by weight silica content are added to 5 g of amorphous extrudates containing 75 % of silica and 25 % of alumina. The so-prepared mixture is heated at
55 140°C for 24 hours. The extrudates are then filtered, washed, dried and roasted at 530°C for 4 hours. Thus,   55
8.64 g of offretite extrudates, adsorbing 8.2 % of cyclohexane at 20°C under 65 mm Hg are obtained. The synthesis parameters were as follows: r_i = 2.55 ; S_1 = 3.8 ; S_2 = 7.18 ; S_3 = 0.0048 ; Q = 1.31 ; r_f = 4.7).

Example 4 : Preparation of erionite
Method 1
    10 g of amorphous extrudates containing 80 % of silica and 20 % of alumina are admixed with 91 ml of water, 4.75 of sodium hydroxide, 2.57 of potassium hydroxide and 6.84 g of amorphous silica. The synthesis
5 parameters are as follows, in accordance with table 11 : $S_1 = 9.1$; $S_2 = 1.81$ mole/1 ; $S_3 = 0$; $Q = 0.68$ g/g (r_i 5
= 3.4). After 24 hours of heating at 140°C, 7.6 g of erionite extrudates whose Si/Al atomic ratio is 3.95, are obtained. As shown by X-ray diffraction and electron microscopy, they are free of L zeolite. After desorption under vacuum at 300°C, this product adsorbs 8.2 % of n-hexane and 1.3 % of cyclohexane.
    The grain by grain crushing strength is 12.4 Newton/mm as compared with 10.1 N/mm for the starting
10 product and the crushing strength in bed is 12.5 MPa as compared with 8.9 MPa for the starting product.   10

Method 2
    5 g of NaY zeolite extrudates of atomic ratio, r_i equal to 2.45, are admixed with 3.45 g of pelletized sodium hydroxide, 2.87 g of potassium hydroxide, 6.56 g of amorphous silica and 50 ml of water. The synthesis
15 parameters are : $S_1 = 10$; $S_2 = 2.75$ moles/liter ; $S_3 = 0$; $Q = 1.31$ g/g. After 36 hours of heating at 170°C, a   15
zeolite of the erionite type is obtained, as indicated by X-ray diffraction ($r_f = 3.5$).

Method 3
    46 g of water, 12.10 g of amorphous silica, 5.42 g of sodium hydroxide and 4.40 g of pelletized potassium
20 hydroxide are added to 2.5 g of NaX zeolite having a Si/Al ratio, r_i, equal to 1.1. After 48 hours of heating at   20
170°C, the extrudates are filtered, washed, dried for 3 hours at 120°C. Thus 4.15 g of erionite, free of L zeolite, with a ratio r_f of 3.2 are obtained. The synthesis parameters were as follows : $S_1 = 16$; $S_2 = 4.65$; $S_3 = 0$; Q
= 4.84.

25 *Method 4*   25
    5 g of kaolin ($r_i = 1$), previously shaped by pelletizing, are admixed with 80 g of water, 22 g of amorphous silica, 10 g of sodium hydroxide and 8 g of potassium hydroxide. After 48 hours of heating at 170°C, the pellets are filtered, washed and dried; their diffraction spectrum corresponds to that of erionite, with a ratio, r_f, of 3.2. The synthesis parameters were as follows: $S_1 = 16$; $S_2 = 4.91$; $S_3 = 0$; $Q = 4.4$.
30   30
Example 5 : Preparation of L zeolite
Method 1
    50 g of 3 A zeolite extrudates ($r_i = 1$) are added to 1020 ml of a solution containing 9.8 % of potassium hydroxide, 0.2 % of sodium hydroxide and 32 % of silica. The preparation parameters are, according to table
35 12 : $S_1 = 20.4$; $S_2 = 2.48$ moles/liter ; $S_3 = 9.27$ g/g.   35
    The mixture is maintained for 18 hours at 160°C in autoclave. The extrudates are then filtered, washed and dried. The diffraction spectrum corresponds to that of L zeolite. The capacity of benzene adsorption at a partial pressure of 70 torrs is 16.5%. The Si/Al ratio r_f is 3.05 and the potassium content 13.0 %.
    The grain by grain crushing strength is 20.9 Newton/mm and the crushing strength in bed of 1.2 MPa,
40 instead of respectively 8.1 Newton/mm and 0.9 MPa for the starting 3 A zeolite. The average size of the   40
grains, as observed by electron microscopy is 0.4 micron as an average.

Method 2
    20 g of kaolin balls are admixed with 52.5 g of potassium hydroxide, 2 g of sodium hydroxide, 110 g of
45 amorphous silica and 150 ml of water. The mixture is brought to 170°C for 24 hours and the balls are then   45
filtered and washed. The diffraction spectrum corresponds to that of L zeolite ($r_f = 3$). The synthesis parameters are as follows : $r_1 = 1$; $S_1 = 7.5$; $S_2 : 6.25$; $S_3 = 0$; $Q = 5.5$.

Method 3   50
50   50 g of amorphous extrudates containing 75 % of silica and 25 % of alumina are admixed with 71 g of potassium hydroxide, 2 g of sodium hydroxide and 230 g of colloidal silica of 30 % by weight silica content. The mixture is heated at 150°C for 2 hours. The extrudates are filtered, washed and dried. The diffraction spectrum corresponds to that of L zeolite ($r_f = 3.2$). The synthesi parameters are as follows: $r_i = 2.55$; $S_1 =$
3.68 ; $S_2 = 7.15$; $S_3 = 0$; $Q = 1.38$.   55
55
Example 6 : Preparation of ferrierite
Method 1
    10 g of Na mordenite extrudates having a Si/Al ratio (r_i) equal to 5 are added to a solution containing 23 ml of 1.08 M tetramethylammonium hydroxide, 4 g of pelletized sodium hydroxide and 44 g of colloidal silica of
60 30 % by weight silica content. After 16 hours of heating at 250°C, the solid phase is filtered, washed and   60
dried. The obtained solid extrudates have a Si/Al ratio of 7.5 and their diffraction spectrum is that of pure ferrierite. The synthesis parameters are as follows : $S_1 = 5.82$; $S_2 = 2.21$; $S_3 = 0.221$; $Q = 1.32$; $r_f = 10.2$.

Method 2

10 g of NaY zeolite extrudates having a Si/Al ratio (r_i) of 2.4 are admixed with 9 g of amorphous silica, 1.7 g of pelletized sodium hydroxide, 1.91 g of pentahydrated tetramethylammonium hydroxide and 45 ml of water. After 16 hours of heating at 250°C, the extrudates are filtered, washed and dried for 3 hours at 120°C.
5 The obtained ferrierite extrudates have a Si/Al ratio (r_f) of 5. The synthesis parameters are as follows : $S_1 =$ 4.5 ; $S_2 = 1.17$; $S_3 = 0.198$; $Q = 0.90$.

Method 3

4 g of colloidal silica of 40 % by weight silica content, 23 ml of a sodium hydroxide molar solution and 1.01
10 g of tetramethylammonium chloride are added to 5 g of amorphous extrudates containing 75 % of silica and 25 % of alumina. The synthesis parameters are the following, in accordance with table 13 : $S_1 = 5.24$; $S_2 =$ 1.0 mole/liter ; $S_3 = 0.286$; $Q = 1.0$ g/g ; $r_i = 2.55$.

After 22 hours of heating at 235°C, 10. 1 g of ferrierite extrudates having a Si/Al ratio (r_f) of 7.9 are obtained.
The crushing strength grain by grain is 24.3 N/mm, as compared to 12.8 for the starting preformed
15 aluminosilicate, and the crushing strength in bed is 1.6 MPa, as compared to 1.1 MPa for the starting product.

Example 7 : Improvement in gas-oil behaviour at cold by means of an offretite.

The zeolite used for this purpose is that prepared according to example 3, by method 1, after exchange with ammonium nitrate, said zeolite containing 2.1 % by weight of potassium. Then 0.4 % by weight of
20 palladium are introduced by exchange with the cationic precursor Pd $(NH_3)_4$ $(NO_3)_2$ or tetrammine palladium nitrate in a solution of 5.10^{-3} M concentration. The product is then roasted in air at 500°C, then reduced under hydrogen in a catalytic unit at 450°C.
A charge is then supplied, whose characteristics are given in table 14.

25

TABLE 14

DISTILLATION			Density (20°)	:	0.876
Initial point	:	220°C	Sulfur (%)	:	1.60 (by weight)
10 %	:	305°C	Nitrogen (ppm)	:	260
50%	:	328°C	Pour point (°C)	:	21
90%	:	362°C	(AFNOR Standard N 0.7.042)		
Final point	:	375°C	Cloud point (°C)	:	21

35   The test is conducted at a pressure of 40 bar with a feeding space velocity (VVH), expressed as charge volume per catalyst volume and per hour, of 1, a H_2/gas-oil volume ratio of 500 liters per liter and a temperature of 410°C. After 20 days or run, the cloud and pour points of the 200⁺ fraction are respectively +3 and 0°C. (The cloud point corresponds to the temperature at which appear the first paraffin crystals ; the pour point corresponds to the solid mass setting temperature).

40

Example 8 : Improvement in the behaviour at cold of a gas-oil with of a ferrierite.

The ferrierite extrudates of example 6, obtained according to method 3, are subjected to two successive cationic exchanges with M solutions of ammonium sulfate, so that the sodium content be lowered to 0.2 % (by weight), followed by an exchange with a 0.1 M nickel acetate solution, so that the nickel content be 2.1 %
45 (by weight). After roasting and reduction, the catalyst is subjected to the same test as that described in example 7, the operating conditions being identical except for the temperature which is 380°C. After 200 hours, the cloud and pour points of the 200⁺ cut are respectively +6 and +3°C.

Example 9 : Hydrocracking over Y zeolite

50   Y zeolite extrudates obtained in Example 1, according to method 1, are subjected to four cationic exchanges in 1.5 M solutions of ammonium chloride so as to bring the sodium content to 1.8 % (by weight), then subjected to roasting at 600°C for 3 hours under static atmosphere, then reexchanged twice so as to bring the sodium content to 0.15% and finally roasted in static atmosphere at 700°C. Then 0.5 % of palladium are introduced by impregnation of the palladium chloride precursor. THe catalyst is then roasted in dry air at
55 500°C and prereduced in the reactor of a hydrocracking pilot unit.
The characteristics of the charge are reported in table 15.

TABLE 15

	DISTILLATION					
	Initial point (°C)	:	201	S (%) by weight	1.2%	
5	50 % point (°C)	:	332			5
	Final point (°C)	:	435	N (ppm)	840	

This charge is preliminarily hydrotreated for removing the major part of nitrogen and sulfur compounds
10 (less than 5 ppm of nitrogen in the effluents) ; the effluents, including H_2S and NH_3, formed in the   10
preliminary hydrotreatment, pass over the zeolite catalyst, in the following conditions :

	- Pressure	(bars)	: 120	
	- Hourly volume velocity	(liter/liter/hour)	: 1.5	
15	- H_2/charge	(gas liter/liquid liter)	: 1 000	15

After 200 hours of run at a temperature of 355°C, a 69 % conversion to products of boiling point lower than
200°C is obtained with a 75% selectivity of weight to C_5 − 180°C cut.
20   20

Example 10 : Hydrocracking over omega zeolite
    Zeolite of Example 2, obtained by method 1, is subjected to cationic exchanges which decrease the sodium
content to 0.5 % by weight. Then 0.3 % of platinum are introduced by exchange with tetrammine platinum
nitrate. The catalyst is roasted at 500°C and prereduced in hydrogen at 500°C in the test unit.
25   The catalyst is subjected to a hydrocracking test on the same hydrotreated charge as in example 8, and in   25
identical conditions except for temperature.
    After 200 hours of run at a temperature of 380°C, the conversion to products of boiling point lower than
220°C amounts to 60 % with a 78 % by weight selectivity to C_5 − 180°C cut.

30 *Example 11* : Methanol conversion over offretite   30
    Zeolite of Example 1, obtained by method 1, is subjected to four successive cationic exchanges in 2M
ammonium nitrate solutions and then dried and roasted at 500°C.
The potassium content is 2.1 %.
    15 cc of extrudates are fed into a reactor and subjected to a test with a methanol charge. Under
35 atmospheric pressure, with a feeding space velocity (VVH, in methanol volume/catalyst volume and per   35
hour), of 2, a temperature of 400°C, the results, after 10 minutes, are those reported in table 16.

TABLE 16

40	CONVERSION	:	CH_3OH	100%		40
	YIELD BY WEIGHT	:	Ethylene	29%		
			Propylene	25%		
			Butene	11%		
			Methane	6%		
45			Ethane	1%		45
			Propane	16%		
			Butane	7%		
			C_5^+	5%		

50   50
Example 12 : Aromatization over L zeolite
    Zeolite of example 5, obtained by method 1, is dipped into a potassium nitrate solution containing 0.3
g/liter of Pt $(NH_3)_4^{++}$ ion. The product is roasted at 450°C and charged with rhenium by impregnation with a
carbonyl rhenium solution $Re_2 (CO)_{10}$. After being charged in a catalytic unit, it is subjected to activation in
55 hydrogen at 450°C, then to a passivation by means of a mixture of 1 % hydrogen sulfide in hydrogen,   55
followed with a purge at 500°C in hydrogen for 8 hours, at a pressure of 10 bars.
    A charge of n-hexane is then introduced in the following conditions : temperature : 470°C, pressure : 3
bars, molar ratio : hydrogen/n-hexane = 3, hourly volume velocity = 3. After 25 hours of run, the n-hexane
conversion is 93 %, the selectivity by weight to benzene is 78% and the selectivity to C_1 − C_5 products 3.1 %.

CLAIMS

1.   A preformed synthetic zeolite selected from Y, omega, offretite, erionite, L and ferrierite zeolites, in which the Si/Al atomic ratio, r_f, is 1.5 to 100, and which has been obtained from at least one preshaped
5 alumino-silicic material selected from natural or synthetic zeolites, amorphous silica-aluminas and clays,   5
said material having a Si/Al atomic ratio, r_i lower than r_f and from 0.5 to 90, said preformed synthetic zeolite being produced by treating said material with a silica-containing product, in the presence of at least one organic or inorganic base selected from lithium oxide, sodium hydroxide, potassium hydroxide and tetraalkylammonium hydroxides, the OH⁻ anion concentration being 0.01 to 10 moles per liter of solution,
10 the molar ratio of tetraalkylammonium cations to (OH)⁻ anions being 0 to 0.5, the amount of silica added to   10
said material being 0.1 to 30 grams per gram of anhydrous aluminosilicic material, the liquid phase/anhydrous aluminosilicic material ratio, by weight, being 2 to 30, and said treatment being conducted at a temperature of from 50 to 200°C, for a period of from 2 hours to about 200 days.

2.   A zeolite according to claim 1, wherein the natural zeolites are selected from the group consisting of
15 analcite, chabazite, clinoptilolite, erionite, faujasite, ferrierite, and mordenite.   15

3.   A zeolite according to claim 2, wherein the zeolite is used as crushed grains.

4.   A zeolite according to claim 1, wherein the synthetic zeolite is selected from A zeolite, X and Y zeolites and mordenite.

5.   A zeolite according to any one of claims 1 to 4, wherein said preformed material is a crystallized zeolite
20 which has been, subjected to an exchange, at least partial, of at least one of its cations with at least one   20
cation other than those originally present in said material, said cation being selected from K⁺, Li⁺, NH₄⁺, H⁺, this cationic exchange being optionally followed by thermal treatment.

6.   A zeolite according to any one of claims 1 to 5, wherein said material is a crystallized zeolite which has already been subjected at least partially to an aluminum removing treatment.

25 7.   A zeolite according to any one of claims 1 to 6 which is "Y Faujasite" zeolite prepared from a material   25
selected from A zeolite, X faujasite, amorphous silica-alumina and kaolin, by treatment of said material with at least one inorganic base selected from sodium hydroxide, potassium hydroxide, lithium oxide, tetraalkylammonium hydroxides, and precursors of said hydroxides, wherein the values r_i, S_1, S_2, S_3, Q, T, t, d, r_f, defined in Table 7 are within the wide ranges indicated in Table 8.

30 8.   A zeolite according to any one of claims 1 to 6, which is an "omega" zeolite prepared from a material   30
selected from A zeolite, X and Y faujasites, amorphous silica-alumina and kaolin, by treatment of said material with at least one inorganic base selected from sodium hydroxide, potassium hydroxide, lithium oxide, tetraalkylammonium hydroxides and precursors of said oxides, wherein the values r_i, S_1, S_2, S_3, Q, T, t, d, r_f, defined in Table 7, are within the wide ranges indicated in Table 9.

35 9.   A zeolite according to any one of claims 1 to 6, which is an "offretite" zeolite prepared from a material   35
selected from A zeolite, X and Y faujasites, amorphous silica-alumina and kaolin, by treatment of said material with at least one inorganic base selected from sodium hydroxide, potassium hydroxide, lithium oxide, tetraalkylammonium hydroxides and precursors of said hydroxides, wherein the values r_i, S_1, S_2, S_3, Q, T, t, d, r_f, defined in Table 7, are within the wide ranges indicated in Table 10.

40 10.   A zeolite according to any one of claims 1 to 6, which is an "erionite" zeolite prepared from a material   40
selected from A zeolite, X and Y faujasites, amorphous silica-alumina and kaolin, by treatment of said material with at least one inorganic base selected from sodium hydroxide, potassium hydroxide, lithium oxide, tetraalkylammonium hydroxides and precursors of said hydroxides, wherein the values r_i, S_1, S_2, S_3, Q, T, t, d, r_f, defined in Table 7 are within the wide ranges indicated in Table 11.

45 11.   A zeolite according to any one of claims 1 to 6, which is an L zeolite prepared from a material selected   45
from A zeolite, X and Y faujasites, amorphous silica-alumina and kaolin, by treatment of said material with at least one inorganic base selected from sodium hydroxide, potassium hydroxide, lithium oxide, tetraalkylammonium hydroxide and precursors of said hydroxides, wherein the values r_i, S_1, S_2, S_3, Q, T, t, d, r_f, defined in Table 7, are within the wide ranges indicated in Table 12.

50 12.   A zeolite according to any one of claims 1 to 6, which is a "ferrierite" zeolite prepared from a material 50
selected from A zeolite, X and Y faujasites, amorphous silica-alumina, mordenite and kaolin, by treatment of said material with at least one inorganic base selected from sodium hydroxide, potassium hydroxide, lithium oxide, tetraalkylammonium hydroxide and precursors of said hydroxides, wherein the values r_i, S_1, S_2, S_3, Q, T, t, d, r_f defined in Table 7 are within the wide ranges indicated in Table 13.

55 13.   A zeolite according to any one of the preceding claims as herein specifically disclosed.   55

14.   A process for the preparation of a zeolite as defined in any one of the preceding claims.

15.   A process for the preparation of a zeolite substantially as herein described.

16.   Use of a preformed zeolite according to any one of claims 1 to 13, in sorption or ionic exchange or as catalyst or catalyst carrier, in heterogeneous catalysis, said zeolite being used alone or as a mixture with at
60 least one other constituent selected from carriers or matrices and the metals or metalloids.   60

17.   Use according to claim 16, wherein the preformed zeolite has been subjected, before use, to at least one pretreatment, said pretreatment being an operation selected from cationic exchange, treatment with at least one organic or inorganic acid and thermal treatment.

18.   The use in catalytic cracking or hydrocracking of a preformed zeolite according to any one of claims 1
to 13, said zeolite being used alone or as a mixture with at least one constituent selected from carriers or
mattrices and metals or metalloids.

19.   Each and every novel product, process, method, apparatus, feature or combination of features   5
substantially as herein described.